

LANSCCE DIVISION RESEARCH REVIEW

Investigating Shape-Memory Alloys and Composites with Neutron-Diffraction Techniques

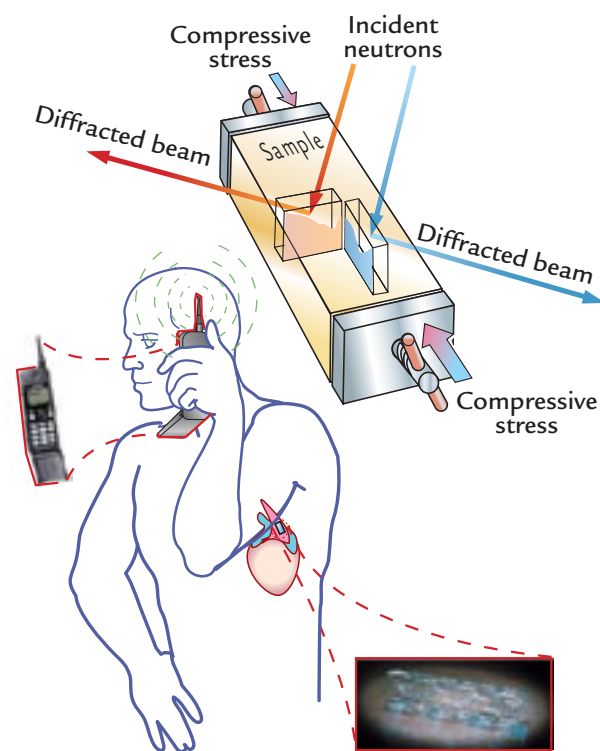
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As the name suggests, the shape-memory effect refers to a phenomenon wherein a material when mechanically deformed and then heated "remembers" and returns to its preset shape. Associated with this behavior is the superelastic/pseudoelastic effect whereby large and completely recoverable strains are generated (i.e., the strains are generated and recovered mechanically rather than thermally). Both of these effects are associated with "martensite" transformation, a first-order displacive transformation usually related to the hardening of steel. When a nickel-titanium (NiTi) shape-memory alloy is mechanically loaded, a stress-induced cubic (austenite) phase to monoclinic (martensite) phase transformation can result in macroscopic strains as high as 8%. On unloading, the martensite becomes unstable and transforms back to austenite with a concomitant macroscopic strain recovery. This phenomenon is called the superelastic/pseudoelastic effect and finds application in, for example, mobile phone antennae, cardiovascular stents, and guidewires.¹ By recording neutron-diffraction spectra during external loading, we can investigate this reversible stress-induced austenite-to-martensite transformation in situ. Such data can provide quantitative phase-specific information on the elastic strain, texture, and volume-fraction evolution. The basic principle of such measurements for strain determination involves using the lattice-plane spacing of grains within the crystal structure as internal strain gauges. For texture, the relative intensities of the diffraction peaks are considered and for phase volume fraction, an integrated intensity of peaks corresponding to a specific phase is used.

Investigating Superelasticity in NiTi and NiTi-TiC

We summarize and synthesize here a systematic study^{2,3} of superelasticity in NiTi subjected to monotonic and cyclic loading and in NiTi-TiC subjected to monotonic, quasi-static loading by the simultaneous acquisition of neutron-diffraction spectra in both samples. The advantage of using neutrons

over x-rays is that the bulk behavior can be investigated in polycrystalline samples (i.e., the 50% transmission thickness in NiTi for Cu-K α x-rays is approximately 9 μm as compared to about 3 cm for thermal neutrons). The spectra were recorded while interrupting the loading and unloading parts of the cycle at the stresses shown in Figs. 2 through 4. The diffraction experiments allowed for the microstructural texture, phase-volume-fraction, and strain changes that were produced during the stress-induced austenite to martensite transformation to be compared to the macroscopic stress-strain response.



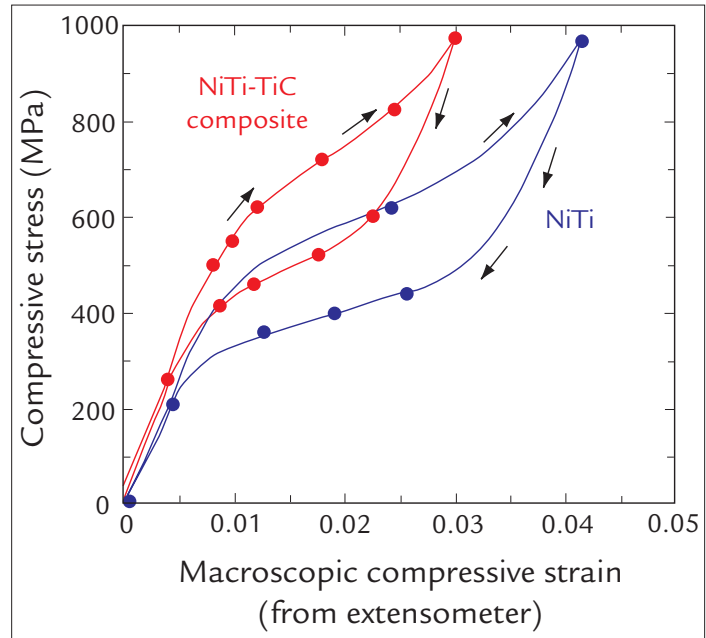
↑ **Fig. 1.** Schematic of the experimental setup at the Lujan Center at LANSCCE, showing the incident neutron beam and two of the three diffracted beams with respect to the loading direction. The irradiation volume is about 1 cm³. The setup was used to study superelastic NiTi, which is used in vascular stents in the human body and in the flexible antennae of mobile telephones. The strain induced by the compressive stress is measured along the scattering vector, which is either parallel to the load axis (i.e., the diffracted beam in red) or perpendicular to the load axis (i.e., the diffracted beam in blue).

Our neutron-diffraction measurements were performed with the Neutron Powder Diffractometer at the Lujan Neutron Scattering Center (Lujan Center) at the Los Alamos Neutron Science Center (LANSCE) (Fig. 1).

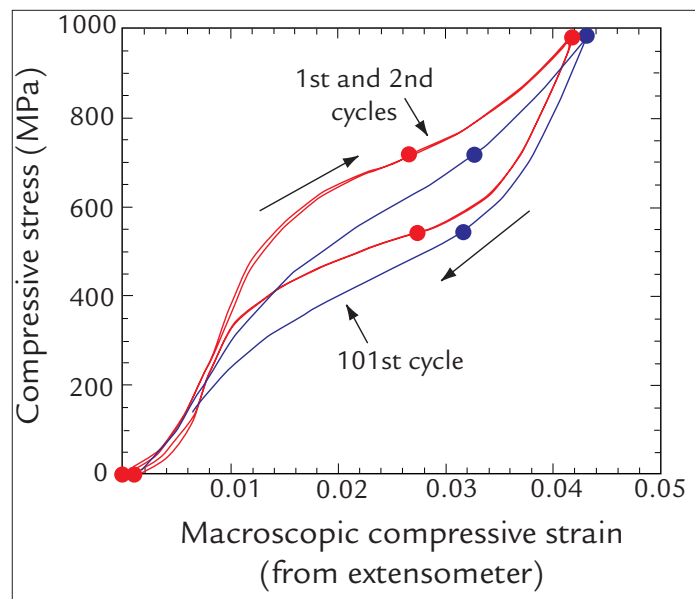
Three series of experiments^{2,3} on hot isostatically processed samples were performed:

- (1) uniaxial compressive loading of NiTi up to 975 MPa and subsequent unloading (Fig. 2),
- (2) cyclic compressive loading and unloading (100 cycles) of NiTi up to 975 MPa (Fig. 3), and
- (3) uniaxial compressive loading of NiTi-TiC up to 975 MPa and subsequent unloading (Fig. 2).

Samples were loaded in compression while neutron-diffraction spectra were simultaneously acquired at three diffraction angles. The loading axis formed an angle of 45° with the incident polychromatic neutron beam, allowing measurements for which the scattering vector was parallel and perpendicular to the loading axis. A third detector was used in backscattering geometry. An extensometer (i.e., a device that measures the change in length of a sample subjected to different loads) was attached to the samples to record macroscopic strain during the experiments. The Rietveld refinement technique, implemented in the Los Alamos National Laboratory code General Structure Analysis System (GSAS),⁴ was used to analyze the neutron-diffraction spectra. In the Rietveld method, the diffraction intensity at every point in the spectrum was determined by adding the calculated background and Bragg scattering intensities corresponding to diffraction peaks. The refinement procedure varied selected parameters (e.g., phase volume fractions, atom positions, and phase texture) until the calculated and measured spectra matched in a least-squares fit. In particular, the procedure incorporated changes in diffraction peak intensities due to texture. A generalized spherical-harmonic-texture description was used to account for the evolving texture from the austenite to martensite phase transformation.



↑ **Fig. 2.** Representative macroscopic compressive stress-strain responses of superelastic NiTi and NiTi-TiC samples during loading and unloading, which were tested in the neutron beam. The symbols on the curves indicated the stresses at which loading was interrupted and neutron-diffraction spectra recorded.



↑ **Fig. 3.** Representative macroscopic compressive stress-strain response of a superelastic NiTi sample during cyclic loading. The symbols on the curves indicate the stresses at which loading was interrupted and neutron-diffraction spectra were recorded.

***In situ* Observation of Microstructural Changes During Transformation**

The generalized spherical-harmonic-texture formulation in Rietveld refinements helped us determine the volume fractions of the austenite and martensite phases that coexisted under an applied stress in NiTi and NiTi-TiC. We observed a linear relationship between the volume of stress-induced martensite and the macroscopic strain generated by the transformation for both NiTi and NiTi-TiC. Both the volume fraction of martensite, which formed at any given applied stress, and the recoverable strain decreased in the presence of TiC particles. This is understandable given that the most favorable variant, in terms of the macroscopic strain, may not be compatible with a non-transforming TiC particle in its proximity and may thus not form.

In the NiTi and NiTi-TiC samples, the overall texture (i.e., preferred orientation of grains) of the martensite decreased with increasing stress. This finding was attributed to favorable orientations of austenite transforming first to martensite and the need for the newly formed martensite to be compatible with the already transformed martensite (and TiC). Upon comparing the texture of martensite formed in the presence and absence of TiC at the same superelastic strain, we discovered that martensite in the presence of TiC was less textured. This is understandable since there are more spatial constraints for the formation of martensite when TiC is present. This situation is analogous to martensite forming at lower strains (where fewer constraints exist) being more textured than the martensite forming at higher stresses (where other martensite plates preclude certain orientations).

Significant discrepancies were observed between the Young's moduli (i.e., the linear relationship between stress and strain in the initial part of the stress-strain curve) for NiTi and NiTi-TiC measured with an extensometer and predictions using single-crystal data and the Eshelby elastic theory.⁵ The differences were attributed to small amounts of austenite transforming to martensite at low stresses, which reduce the apparent Young's moduli. In contrast to the above macroscopic data, the modulus of austenite in NiTi measured by neutron diffraction (from the slope of applied stress versus elastic strain response) compared well to moduli predicted using single-crystal data. The applied stress at which austenite transforms to martensite and back to austenite increased in the presence of TiC particles. For both NiTi and NiTi-TiC, the elastic lattice strain in the

austenite remained linear with respect to the applied stress even when significant volume fractions of austenite had transformed to martensite, but showed some nonlinearity at higher applied stress. This load transfer coupled with the stress hysteresis results in strains in the austenite during unloading being somewhat larger than strains during loading for the same stress. For the NiTi-TiC composite, we observed good agreement in the phase strains predicted by the Eshelby elastic theory and those measured with neutron diffraction. In general, the self-accommodating nature of the stress-induced martensite almost eliminated the mismatch with the TiC particles and the transforming austenite. Additional anisotropy introduced by strain redistribution caused by the transformation was reflected in changes in the anisotropic component of the strain of the austenite phase in NiTi-TiC.

For the case of cyclic loading, the change in macroscopic stress-strain behavior at intermediate stresses where martensite and austenite coexist was found to result from an increase in both volume fraction and texture in the stress-induced martensite. The average elastic strain in austenite remained mostly unchanged at intermediate stresses, but the isotropic and anisotropic components of the strain in austenite redistributed themselves. The residual elastic strain present after unloading in austenite also evolved during cycling. These phenomenological observations shed light on the materials evolution occurring during repeated reversible stress-induced transformation in superelastic NiTi, which is important both during mechanical training (i.e., process of stabilization prior to actual use) of NiTi devices and during their subsequent use.

Ongoing Work

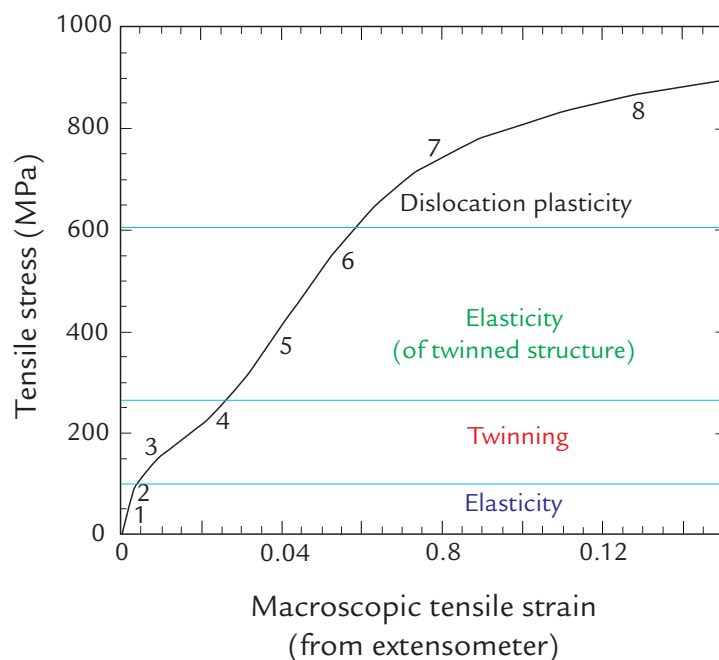
The martensite phase in NiTi consists of 24 "variants" with varying crystallographic orientations and can deform by twinning, producing macroscopic tensile strains as high as 8%. (Twinning is an imperfection in polycrystals involving the intergrowth of two or more polycrystal grains so that each grain in a twinned system is a reflected image of its neighbor. In essence, twinning is a special type of grain boundary defect where a polycrystal grain is joined to its mirror image.) Heating results in a phase transformation to the austenite phase and recovery of all the macroscopic strain accumulated by twinning, a phenomenon known as shape-memory. Due to their ability to work against large forces during this strain recovery, shape-memory alloys are widely used as actuators in engineering applications. In 2001, we performed *in situ* neutron diffraction during tensile

and compressive loading of shape-memory martensitic NiTi. Our objective was to follow deformation twinning as a function of the applied external load and to relate the texture and internal strain evolution (from diffraction data) with macroscopic strain data (obtained from an extensometer). Fig. 4 shows the typical stress-strain response of shape-memory NiTi. The various numbers indicate the stress levels at which loading was interrupted and neutron-diffraction spectra obtained. A holding period of about 6 hours was used at each stress level. Numbers 1 and 2 represent elastic loading, 3 and 4 represent twinning deformation, and 5 and 6 represent elastic deformation of the twinned martensite. This is followed by yielding due to dislocation plasticity and strain-hardening (7 and 8). Because of the asymmetric nature of the stress-strain curve with respect to tension and compression, we performed two series of experiments using compressive and tensile loads. We do not fully understand the deformation mechanisms indicated in Fig. 4, and a comprehensive thermomechanical model describing constitutive behavior (i.e., the material response to stress and strain) is still unavailable. The ability to follow the texture and strain evolution during these stages and examine the micromechanical and microstructural changes using neutrons will therefore be of significant scientific and engineering interest. The results obtained at LANSCE are currently being evaluated using the methodology developed in Reference 6.

References

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Nearly 5 years ago, when John Browne became the Laboratory's Program Director for LANSCE and Energy Research (LER) programs, the task of redirecting the activity of the Technical Area 53 mesa from meson physics to neutron science seemed a daunting one. In those early days, John and I wrote a program plan that articulated the case for neutron science playing a central role in the U.S. Stockpile



↑ **Fig. 4.** Tensile stress-strain curve of shape-memory NiTi. The numbers indicate the stress levels at which loading was interrupted and neutron-diffraction spectra were obtained. The associated dominant deformation mechanisms are also indicated.

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